

EXPERIMENTAL STUDIES OF S-ROCK INTERACTIONS. IMPLICATIONS FOR IO. J. S. Goreva, D. S. Burnett, *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena.*

Abstract. Laboratory experiments have been carried out in order to test whether the interaction of S_2 -gas and a mixture of S_2 and SO_2 gases with silicate materials can produce Na-S compounds on the surface of Io. Experiments were performed in sealed SiO_2 -glass tubes with slices of different silicate glasses and elemental S. Temperature was varied between $950^\circ C$ and $1036^\circ C$ and S-gas pressure between 5 and 10 atmosphere. Interaction with S_2 -gas produced different sulfides in soda-lime glass, chondrule glass, Kilauea alkali basalt (KAB) and obsidian. Na-S phases were recognized on the surface of soda-lime and obsidian samples, Fe-sulfides were formed in KAB and obsidian, traces of dissolved sulfur were observed in a chondrule glass. In the presence of mixed S_2 and SO_2 gases, nepheline-albite (Ne-Ab) glass and KAB produced Na-S phase and Fe-sulfide respectively.

According to these experimental results, interactions between silicate materials and S_2 -gas or $S_2 + SO_2$ gas mixtures at high temperatures appear to be a plausible mechanism for extraction of Na from silicate materials. These results along with previously studied SO_2 -silicate interactions should be considered as mechanisms for the formation of Na-S phase on the surface of Io.

Introduction. Iogenic O, S, and Na ions dominate the Jovian magnetosphere. K is also observed in the atomic cloud surrounding Io with K/Na roughly 0.5 atomic [1]. This is relatively little direct information about the chemistry of Io; however, the dominance of Na, when considered in the light of the elements that are not observed, provides significant constraints on Io geological processes. Significant upper limits show that the densities of Si, Mg, and Fe ions in the Io torus are much less than Na [1]. Similarly, upper limits on Ca and Mg in the atomic cloud [1; M. Brown, Caltech, pers. comm.] indicate Ca/Na and Mg/Na ratios much less than chondritic. The iogenic ions are derived by sputtering, most likely of the satellite surface, but sputtering of volcanic aerosol particles cannot completely be ruled out. Regardless, the observed large enrichments of Na relative to other lithophile elements cannot be due to sputtering, but must represent unique Io geochemical processes. Our research is focused on constraining the mechanisms for Na enhancement but also on developing the implications of the existence of the Na enrichment for Io geology and geochemistry. For example, making the plausible assumption (valid every place else we know about in the solar system) that Na brought into Io initially in silicate phases, the observed Na enrichment must involve extraction of Na from silicates; however, as indicated below, there are significant constraints on the rock types that can serve as sources for the observed Na enhancements.

One of the plausible hypotheses for the nature of the Na-bearing phases is the formation of Na-sulfates and sulfides as a result of interaction of sulfur and sulfur oxides with silicate material [2, 3, 4].

In this work we extended the experimental study of S-rock interaction for a number of natural Na-bearing silicate materials and provided a number of experiments in the presence of a mixture of S_2 and SO_2 gases.

Experimental. Experiments were carried out in evacuated SiO_2 -tubes with slices of silicate glasses of different compositions. Sulfur (99.95% pure) was added to produce desired gas pressures at given temperatures. To produce a mixture of S_2 and SO_2 -gases, samples were sealed in air. Partial pressure of SO_2 and S_2 gases was ~ 1 atm and ~ 4.5 atm respectively. The estimated total pressure inside the capsule was 9 to 10 atm at $1036^\circ C$. Samples were placed in a horizontal preheated furnace and then air-quenched after runs of 3 to 16 days.

After completion of the experiments, the capsules were broken and placed into a Scanning Electron Microscope (SEM) for analysis. To prevent oxidation total exposure did not exceed 5 min. The SEM was used for qualitative phase identification and textural observations.

Results. Products of sulfur-silicate reactions appear on the surface of silicate chips as blobs, stringers and rosettes. These phases usually were too small for quantitative analyses, so we will call them "Na-S phase", being aware that oxygen might be also present. Experimental conditions and results, along with a summary of previous experiments, are given in the table. We will further describe the results of silicate interactions with (1) S-gas and (2) S_2+SO_2 -mixture.

(1) Interaction of silicates with elemental sulfur. Soda-lime glass ($950^\circ C$, $P(S_2)=5$ atm., 4 days) produced globular rosettes (~ 10 mm diameter), and thin (~ 1 mm wide), long (up to 100 mm) fibers of Na-S phases. Morphologies are consistent with those observed by [3], who identified their products as Na-sulfides. Chondrule glass ($950^\circ C$, $P(S_2)=10$ atm., 16 days) did not show extensive reaction, although all SEM spectra showed traces of S. Mono obsidian ($950^\circ C$, $P(S_2)=10$ atm., 16 days) showed two different products of reaction: (1) rather extensive semicircular flat Fe-S aggregates roughly $20 \mu m$ in diameter, (2) rare 100-200 μm long, few μm wide, dendritic stringers enriched in Na-S with small amounts of K, Mn, Fe and Zn. On the surface of Kilauea alkali basalt ($950^\circ C$, $P(S_2)=10$ atm., 16 days), yellowish-brown bright reflective 5-20 μm round droplets of Fe-sulfide were observed. There is no evidence of Na-S phases in this sample.

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Summary of S-rock experiments.				
	SO ₃ ^a (Johnson & Burnett, 1993)	SO ₂ ^b (Burnett et al., 1996)	S ₂ (this work; *Johnson & Burnett, 1990)	S ₂ +SO ₂ ^f (this work)
Albite	K-Na-Al-sulfate	no reaction	no reaction ^{c*} no reaction ^e	---
AbOr glass	K-Al-sulfate; minor Na	no reaction	---	no reaction
Mono obsidian	Na-K-Al-sulfate; trace Fe	rare Fe-S	Fe- sulfide + Na-rich sulfide with traces Mn, Fe, Zn ^e	no reaction
Soda-lime	Na-sulfate	Na-S phase	Na-K sulfides ^{c*} ; Na sulfides ^d	---
AbAnDi glass	two sulfates:CaSO ₄ + Na-rich sulfate with Ca, K and Al	Ca-S crystals (anh.?) Na-Ca-liquid?	---	---
Chondrule glass	two sulfates: CaSO ₄ + Na-Mg-Ca-sulfate	Ca-S phase	rare Ca-S phase ^e	---
NeAb glass	---	---	---	Na-S phase (sulfide?)
KAB basalt	two sulfates: CaSO ₄ +Na-Ca- Mg sulfate; trace K, Fe	no reaction	Fe-sulfide ^e	Fe-sulfide

^a SO₂/O₂=1 gas mixture, total pressure ~3atm, 850°C, 7 days; ^b SO₂-gas pressure ~3-5atm, 850°C, 7-26 days; ^c S-gas pressure ~35atm, 850°C, 3 to 22 days; ^d S-gas pressure ~5 atm, 950°C, 4 days; ^e S-gas pressure ~10atm, 950°C, 16 days; ^f sealed in air, S-enough for 5 atm. After calculation - S-gas ~4.5atm, SO₂-gas ~1atm; total P~9atm, 1036C, 5-7 days.

(2) *Interaction of silicates with mixture of S₂-SO₂*. *Nepheline-Albite* (1036°C, P(S₂)~4.5 atm, P(SO₂) ~1 atm, P_{total} ~9 atm, 7 days) sample produced two Na-S products: (1) bubbles of 1-5 μm diameter, and (2) stringers few microns wide and up to 50 μm long. Unfortunately these features collapsed under the X-ray beam, making their analysis very difficult. *Kilauea alkali basalt* (1036°C, P(S₂)~4.5 atm, P(SO₂)~1 atm, P_{total} ~9 atm, 5 days) showed only Fe-sulfides in the experiment as with pure S-gas.

Discussion. The results presented above show that Na-S rich phases were formed on soda-lime glass, obsidian glass and NeAb compositions. Fe-S phases (presumably sulfides) were formed on KAB and obsidian samples. Chondrule glass did not show recognizable products of reaction, although SEM spectra showed some dissolved S in the glass. Although better experiments are required to define the reaction products, we were able to show that S₂ and S₂-SO₂ - rock interactions should be considered as plausible mechanism for the formation of Na-S phases in the ionian crust. This summary is consistent with previously studied SO₂-silicate interactions [3, 4, 5].

There are no Na-sulfates or Na-sulfides of igneous origin known in terrestrial magmatic systems, although Na₂SO₄ is described in evaporites and fumarolic deposits. On Io, Na sulfides and sulfates could be formed when SO₂ and S₂ are trapped by surface magma flows or in volcanic tubes. A separate issue is how could Na-S phases could be brought to the surface of Io. Lunine and Stevenson [2] proposed a model of convection of ionian sulfur lakes as a delivery mechanism for Na-sulfides. Other possibilities

include the transport of Na-sulfates (and/or sulfides) during fumarolic activities or entrainment of Na-S phases with volcanic eruptions.

In experiments involving Fe-bearing materials, Fe-S reactions seem to be more likely to occur compared to Na-S reactions. This result is broadly analogous to a positive correlation of sulfur and Fe contents in reduced melts (e.g.6). If Io has a peridotite-like mantle [e.g. 7], its melting would produce Fe-rich magmas which interacting with sulfur in reduced conditions form Fe-sulfides. No Fe has been observed on the surface of Io, therefore we are facing two possibilities: (1) magma-S interactions occur on Io under oxidizing conditions, when all Fe is bounded up in Fe-oxides, or (2) S-magma interactions occur in reduced conditions for which the lack of Fe in magmas erupting on the surface of Io suggests the presence of a highly differentiated, Fe-free ionian crust. The generation over geologic time of such crust is consistent with the extremely intense magmatism observed on Io.

Our work showed that in principle, Na can be extracted from Fe-free silicates with S₂ (or S₂+SO₂). Future studies will be aimed in producing enough reactions products to allow determination of specific phases. This goal will be achieved by increasing temperature, pressure and duration of experiments.

References: [1] Trafan (1976), *Icarus*,27. [2] Lunine & Stevenson (1985) *Icarus*, 64. [3] Johnson & Burnett (1990) *GRL*, 17. [4] Johnson & Burnett (1993) *JGR*, 98. [5] Burnett et al. (1996) subm. to *JGR Planets*. [6] Poulson et al. (1990) *Chem.Geol.*, 85. [7] Smith et al. (1979) *Nature*, 280.